MICELLE TO LAMELLAR AGGREGATE TRANSITION OF AN ANIONIC SURFACTANT IN DILUTE AQUEOUS-SOLUTION INDUCED BY ALKALI-METAL CHLORIDE AND TETRAALKYLAMMONIUM CHLORIDE SALTS

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Micelle to Lamellar Aggregate Transition of an Anionic Surfactant in Dilute Aqueous Solution Induced by Alkali Metal Chloride and Tetraalkylammonium Chloride Salts

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Micelles of the anionic surfactant sodium dodecylbenzenesulfonate (NaDoBS) in dilute aqueous solution can be transformed into lamellar aggregates by the addition of alkali metal chloride (LiCl to CsCl) and tetraalkylammonium chloride (alkyl is methyl or *n*-butyl) salts. Depending on the type of cation, concentration of salt, and isomeric purity of the alkyl chain of the surfactant, different types of phases are observed: large unilamellar vesicles, multivesicular vesicles, and flocculated multilamellar vesicles (lamellar droplets). Over limited concentration ranges, some salts induce phase separation in a surfactant-rich and a surfactant-lean phase. The formation of the different phases was monitored by turbidity and fluorescence depolarization measurements, whereas the phases were characterized by light microscopy, freeze-fracture electron microscopy, and confocal scanning laser microscopy. Thermodynamic aspects of aggregation, in particular the counterion binding characteristics, were studied by microcalorimetry and conductivity. On a molecular level, the packing in a lamellar array can be explained largely in terms of a change in counterion binding and, to a lesser extent, by a decrease of the hydration of the headgroup and the counterion. A better counterion binding is facilitated by a less hydrated cation or by an increase of the electrolyte concentration. The formation of different types of lamellar aggregates is due to different types of interactions between lamellar layers or between aggregates: largely repulsive for stable dispersions of unilamellar vesicles to attractive down to short distances for the flocculated lamellar droplets.

Introduction

The aggregation of surfactants in a lamellar array can be facilitated if one of the following requirements is met. First of all, a high surfactant concentration in water often leads to a lyotropic lamellar liquid-crystalline phase. Numerous phase diagrams can be listed, where, as a function of composition and/or temperature, a lamellar phase is observed.[1,2] Double-tailed amphiphiles usually form bilayer sheets, as their most hydrated state allows the molecules to pack only in a lamellar arrangement. Upon closing, these sheets form vesicles.[3-5] Lamellar aggregates are also formed from delicate mixtures of anionic and cationic surfactants in water[6] or mixtures of ionic surfactants and long-chain alcohols in water[7] or electrolyte solution.[8] Some surfactant molecules in aqueous solution are spontaneously transformed from micelles into a lamellar array in the presence of a high salt concentration. On a molecular scale, this change in aggregate morphology is facilitated by an increase in counterion binding and dehydration of the surfactant headgroups and bound counterions. On a larger scale, interactions between lamellae occur, leading to the formation of either unilamellar vesicles (small or large) or multilayered systems (oligo- and multilamellar vesicles, lamellar droplets, or a continuous lamellar phase, L_α). The induction of a lamellar arrangement of surfactant molecules by salts finds an important commercial application in liquid laundry detergents.[9-11]

In an attempt to elucidate the mechanism of this transition from micelle to lamellar aggregate, we previously reported on the sodium citrate-induced transition found in dilute mixtures of an anionic surfactant, polydisperse sodium dodecylbenzenesulfonate (NaDoBS), and a nonionic surfactant of the poly(ethylene oxide) alkyl monoether type.[10] In the present study we describe the behavior of only the anionic NaDoBS in dilute solutions as a function of salt concentration, where the salt is systematically varied along the lyotropic series (LiCl, NaCl, KCl, RbCl, CsCl) and extended with two tetraalkylammonium chloride salts (TAACl, alkyl being methyl or *n*-butyl). The reason for this structural variation originates from the fact that the cation hydration alters dramatically along this series, from highly hydrated for Li^+ to weakly hydrated for Cs^+ to more hydrophobically hydrated for the TAA^+ ions. As a rule of thumb, less hydrated ions lead to higher counterion binding in surfactant aggregates.[12,13] This will have drastic consequences for the transition into a lamellar arrangement of the surfactant molecules. Several reports in the literature indicate that the change from Na^+ to other alkali metal cations, especially Cs^+, induces changes in aggregates of anionic surfactants, which are related to the hydration characteristics of the specific counterions.[13-17] A similar role is played by anions in the aggregation behavior of

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alkyltrimethylammonium salts in water,[12b] where changing from the common bromide counterion to the better hydrated hydroxide ion leads to smaller micelles with higher curvature.

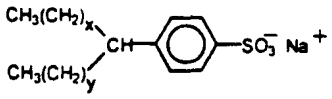
Also the isomeric purity of the hydrophobic tail of the surfactant can have a profound influence on the aggregation behavior. This will be illustrated by compairing the aggregation behavior of the polydisperse NaDoBS with that of the isomerically pure 5/6 sodium dodecylbenzenesulfonate.

In addition to the rearrangement on a molecular scale, the interactions between aggregates or between bilayers are influenced by the nature of the interaggregate or the interbilayer medium, in this case, type of salt and its concentration. The interactions between bilayers (and aggregates in general) are governed by several factors, as reviewed by Israelachvili.[18,19] These interactions are comprised of an attractive van der Waals force, acting on any two bodies over a different medium, and, on the repulsion side, involve the electrical double layer forces. On a shorter distance, the hydration force is considered, as proposed by Rand and Parsegian,[20] but these effects are controversial.[21] Repulsions which are due to thermally-induced motions of the surfactant molecules and of the bilayers are the steric forces, divided in three different types: protrusion repulsion[21] and peristaltic membrane motions,[22] both acting on rather small distances, and (Helfrich) undulation repulsion,[23] which can act over substantially larger distances for flexible bilayers.

This study aims at explaining what are the physical factors determining the aggregation behavior of the anionic surfactant sodium dodecylbenzenesulfonate (NaDoBS) in different aqueous salt solutions.

Experimental Section

Materials. The anionic surfactant was a commercial dodecylbenzenesulfonic acid (HDoBS, MARLON AS3, Hüls, 98.3% pure, provided by Unilever Research Laboratory, Vlaardingen, The Netherlands) with an average composition as sketched, containing a few tenths of a percent sulfuric acid and the remaining part is non-surface-active organic material.



$x + y = 8.3$

Solutions were adjusted to a pH of approximately 7 with sodium hydroxide, yielding an aqueous solution of the sodium salt (NaDoBS). The solid NaDoBS was also prepared by reaction of HDoBS with sodium ethoxide in ethanol and recrystallization from 2-propanol/acetonitrile. Under these conditions, possibly a small fractionation has occured. (Elemental analysis $C_{17.3}H_{36.6}O_3SNa$ in weight percentage: Calcd: C, 62.0; H, 8.4; S, 9.2; Na, 6.6. Found: C, 61.7; H, 8.4; S, 9.5; Na, 7.3. The analysis is probably affected by the presence of trace amounts of Na_2SO_4.) The cesium salt and the tetramethylammonium salt (TMA) were prepared by neutralization with CsOH or TMAOH (both from Aldrich), respectively, in absolute ethanol and recrystallization from ethanol or petrolium ether, respectively. Pure 5/6 NaDoBS (provided by Unilever Research Laboratory, Port Sunlight, U.K.) is an isomerically pure sodium dodecylbenzenesulfonate with x = 4 and y = 5, and was used as received. The salts, LiCl, NaCl, KCl, RbCl, CsCl (all Merck), and tetra-*n*-butylammonium chloride (TBuACl) (Fluka), were used as received. TMACl (Aldrich) was dissolved in ethanol, filtered, and precipitated in acetone. Fluorescent probes *trans,trans,trans*-1,6-diphenyl-1,3,5-hexatriene (DPH, Janssen Chimica, Beerse, Belgium)) and Rhodamine-B (Merck) were used as received. Water used to prepare all solutions was demineralized and double distilled in an all-quartz distillation set up.

Sample Preparation. Samples were prepared by either dissolving approximately 4 mmol of NaDoBS (solid) per kg of water (*m*) or diluting a concentrated HDoBS solution, neutralized by NaOH, to approximately 4 m*m*. No differences in phase behavior were found for the surfactants obtained by the two methods of preparation. The phase behavior of NaDoBS in dilute solution was studied by turbidity and fluorescence depolarization measurements. Solutions were labeled with DPH by vortexing the surfactant solution for at least 10 min over a film of fluorophore, made by evaporation of the solvent from a solution of DPH in THF, under a stream of nitrogen. The fluorophore/ surfactant ratio was about 1:10000. Fluorescence cuvettes were filled with 2 g of surfactant solution. Then the salt concentration was increased stepwise by addition of the particular salt in small, precisely weighed amounts, either as a solid or, when phase changes occur over short salt concentration ranges, in a concentrated solution of known composition. After dissolution of the salt and homogenization, the turbidity and fluorescence depolarization value were determined immediately (see below). Samples were kept at ambient temperature. Refractive indices of 1.0 *m* XCl salt solutions were measured with a conventional Zeiss refractometer at 25 °C.

Turbidity Measurements. Turbidity measurements were performed at 25 °C with a Philips PU 8740 UV/VIS spectrophotometer. Turbidity is expressed as the optical density at 400 nm in absorption units.

Fluorescence Depolarization. An SLM Aminco SPF-500C spectrofluorometer equipped with a polarization device was used for fluorescence depolarization experiments. Measurements were performed as described before.[10] The excitation wavelength was 360 nm; emission was determined at 428 nm.

Light Microscopy. After the occurence of the different phases was monitored by turbidity and fluorescence depolarization studies, specific samples were examined by light microscopy with a Zeiss Axioskop or a Zeiss Axioplan light microscope equipped with an automatic photocamera, using the bright field, the phase contrast (Axioplan), and the crossed polars mode. To prevent the collapse of aggregates, a thin strip of Parafilm was employed in several cases as a spacer between the microscope slide and the coverglass. In this way the possibility was created to observe the structures in unperturbed surroundings. A disadvantage of the method is that the aggregates above and below the plane of focus can obscure the image.

Electron Microscopy. Freeze-fracture replicas were made as described previously;[10] samples were examined in a Philips EM 201 electron microscope, operating at 60 kV.

Confocal Scanning Laser Microscopy. Several solutions were examined by confocal scanning laser microscopy (CSLM). The procedure has been described before;[10] samples were stained with Rhodamine-B analogously to the solutions employed for fluorescence depolarization (see above).

Microcalorimetry. The enthalpy of aggregation (ΔH_{aggr}) and the critical aggregation concentration (cac) were determined using a MicroCal Omega titration microcalorimeter (MicroCal, Inc., Northampton, MA). Procedures have been described in detail by Bijma *et al.*[24] In short, a degassed solution of known surfactant concentration (using the NaDoBS obtained after recrystallization) in the particular continuous phase, water or electrolyte solution (roughly 10 times the cac), was injected in fixed increments (usually 4 *m*L) into a reservoir with overflow, containing 1.3249

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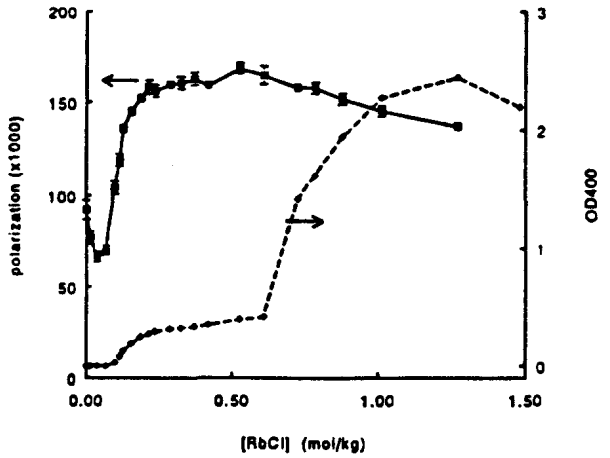

Figure 1. Fluorescence depolarization and turbidity (optical density at 400 nm) of a 4 m*m* NaDoBS solution in water as a function of RbCl concentration: ■, polarization, left axis; ◆, turbidity, right axis.

mL of degassed continuous phase at 25.0 ± 0.1 °C. After each injection the instrument records the heat released or dissipated by the solution, in this case the breakup of aggregates and dilution. ΔH_{aggr} and the cac can be extracted from the raw data analogously to the method described by van Os *et al.*[25] Notice that concentrations for microcalorimetry and conductivity studies are in mol/L (molar) whereas all the other concentrations are expressed in mol/kg (molal). Measurements were performed in duplicate or sometimes in triplicate.

Conductometry. Critical micelle concentrations (cmc) and the fraction of counterion binding, *b*, were determined by a Wayne Kerr Autobalance Universal Bridge B 642 conductometer. A solution of NaDoBS, with known concentration in water or 3.5 mM salt solutions, was injected in fixed increments into the isotonic continuous phase at 25.0 ± 0.1 °C. After homogenization the conductance was measured (in mS). Concentrations were corrected for volume changes. The cmc was taken from the intersect of the lines fitted through an array of points before and an array of points after the break in a conductivity versus concentration plot. *b* was calculated as 1 - (slope after/slope before breakpoint). cmc values in electrolyte concentrations higher than 3.5 mM cannot be measured by conductivity, because the variation in conductivity is too small compared to the scale of the instrument necessary to measure conductance.

Results

The addition of salts to a solution of NaDoBS in water induces different types of surfactant aggregates, easily observable in solutions as dilute as 4 m*m* (only twice the cmc in water). These changes can be probed when the salts are added in small steps by monitoring the turbidity and the fluorescence depolarization of a fluorescent probe (DPH) bound to the surfactant assembly. As an example, the behavior of RbCl is depicted in Figure 1. The DPH fluorescence depolarization, which reflects the microviscosity of the hydrophobic surroundings of the probe,[26,27] and the turbidity of the same sample are combined in one graph. Following the turbidity line, the sample turns slightly turbid at 0.1 *m* RbCl and becomes very turbid at 0.6 *m*. These changes in turbidity as a function of salt concentration mark the boundaries of areas in which different types of aggregates are present. These aggregates are characterized by several microscopy techniques (see below). The turbidity changes correspond to the micelle-to-unilamellar aggregate and the unilamellar-to-multilamellar aggregate transitions, respectively. This picture is supported by the changes of the fluorescence depolarization value *P* as a function of salt concentration. Usually, in the experimental set up used here, *P* is larger than 0.3 for a bilayer in its gel (or frozen) state (L_b), between 0.1 and 0.3 for a bilayer in the liquid crystalline state (L_α), and still lower for a micellar aggregate (<0.1), depending on the viscosity of the microenvironment of the probe and the possibility for the probe to rotate during the lifetime of its excited state. Above 0.1 *m* RbCl, *P* increases drastically, which is due to the formation of lamellar aggregates, in which the probe is much more hindered in its movement by the lamellar packing of the surfactant molecules. The second transition from unilamellar to multilamellar does not alter the microsurroundings of the probe. The slight decrease of *P* beyond 0.6 *m* RbCl is due to the fact that turbid solutions depolarize the light by scattering, and consequently, the values become less reliable.

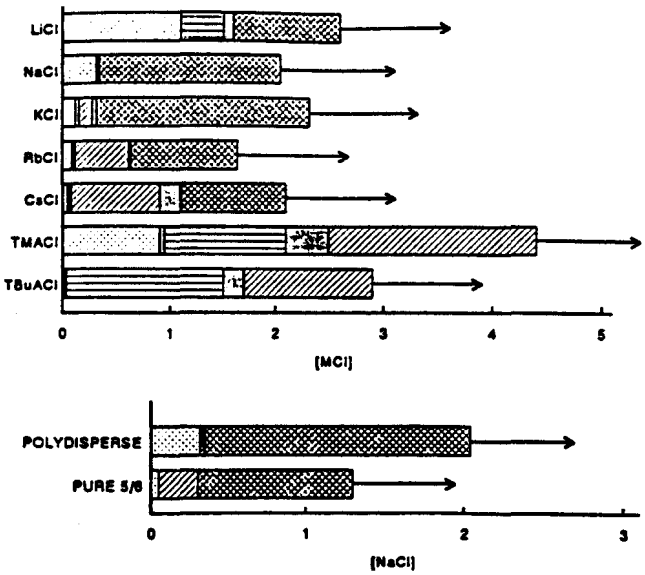

Figure 2. (A) Phase behavior of a 4 m*m* NaDoBS solution in water in the presence of different electrolytes, or formally, routes in the NaDoBS/XCl/water phase diagram. (B) Phase behavior of 4 m*m* solutions of isomerically pure 5/6 NaDoBS and polydisperse NaDoBS as a function of NaCl concentration: dotted, micellar phase; hatched, dispersion of unilamellar aggregates; crosshatched, flocculated multilamellar aggregates separated from the isotropic electrolyte solution; horizontal lines, separation in a surfactant-rich and a surfactant-lean phase; dark gray, transition from one state to another, both states occurring at the same time.

The effects of the other salts on the phase behavior of dilute NaDoBS solutions in water are outlined in Figure 2A. In fact these bars are routes in the NaDoBS/XCl/ water phase diagram at a single temperature, starting on the NaDoBS-water axis, rather close to the 100% water corner, and running toward the XCl corner. The arrows only mean that at that point the current type of NaDoBS aggregate would remain the same on further salt addition, but the measurements were stopped. The unilamellar and multilamellar aggregates are characterized by light microscopy and (in several cases) by freeze-fracture electron microscopy (FFEM) (see Figures 3A,C,D and 4A,B).

Multilamellar aggregates appear for all the alkali metal cations. However, the system passes through different preceding stages. In the case of LiCl, a phase separation occurs in a surfactant-rich and a surfactant-lean phase in the concentration range between 1.1 and 1.6 *m*. Neither light microscopy, nor FFEM, nor confocal scanning laser

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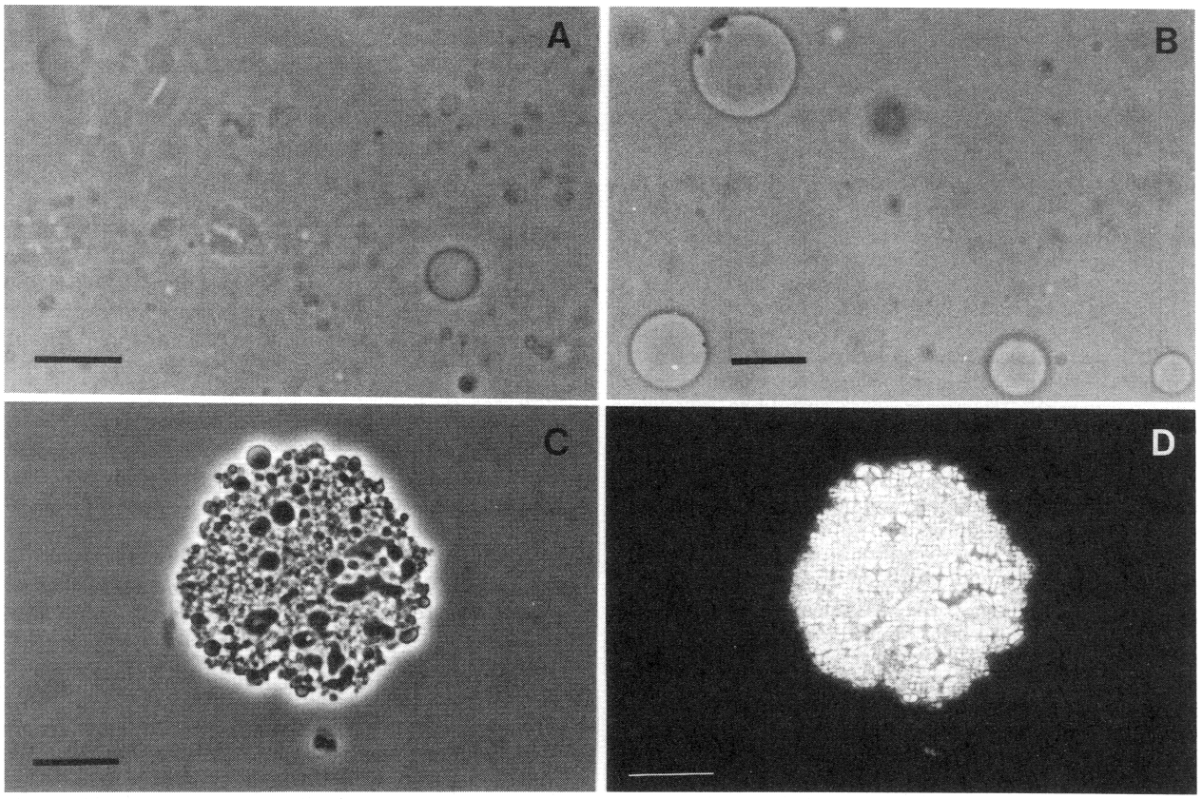

Figure 3. Light microscopy micrographs of (A) 4 m*m* NaDoBS in 0.3 *m* CsCl, phase contrast; (B) same as (A) but in 3.3 *m* TMACl, bright field, both showing large unilamellar vesicles; (C) and (D) flocculated lamellar droplets (multilamellar vesicles) of NaDoBS in 1.2 *m* RbCl (clearly visible from the Maltese crosses in (D)), phase contrast and crossed polars, respectively. The bar represents 10 *m*m (graph A, C, and D) or 25 *m*m (graph B).

microscopy (CSLM) reveals a clear picture for the packing of surfactant molecules in this surfactant-rich phase.

NaCl induces the formation of multilamellar aggregates straight after the micellar phase. There is a small but significant increase in *P* between 0.2 and 0.35 *m*, before the multilamellar stage is entered, which can be attributed to a tighter packing of surfactant molecules leading to micelles with different geometry (for instance, with a more rod- or disk-like shape). A similar change in shape has been observed by light scattering.[28] This feature is observed for the LiCl solutions as well.

The other alkali metal chlorides induce the formation of unilamellar aggregates, before higher salt concentrations turn these structures into multilamellar aggregates. Large unilamellar vesicles are observed by light microscopy, although these are often too small and moving too fast to catch them by photography; see Figure 3A. Figure 4A shows an FFEM micrograph of these vesicles. These unilamellar aggregates are colloidally fairly stable and physically rather instable since some sedimentation occurs slowly after several days, the unilamellar character of the aggregates remaining intact. The final multilamellar stage is physically and colloidally much less stable, and the aggregates flocculate and cream completely from the electrolyte solution within an hour. The transition to multilamellar aggregates becomes less cooperative going toward CsCl. Addition of urea breaks down the multilamellar aggregates into micelles. This interesting phenomenon has not been examined in more detail.

Compared to the commercial, rather polydisperse NaDoBS, the isomerically pure 5/6 NaDoBS forms salt-induced lamellar aggregates at much lower NaCl concentrations than the polydisperse type; see Figure 2B. Most remarkable is that initially, at 0.05 *m* NaCl, unilamellar aggregates are formed, characterized by a rather high *P* and a rather low turbidity. At 0.25 *m* NaCl, multilamellar aggregates form, which flocculate and precipitate from the solution, as indicated by a sharp increase in turbidity. Again, *P* does not change at the transition from unilamellar to multilamellar aggregates.

Tetraalkylammonium chloride salts (alkyl = methyl or *n*-butyl) have a peculiar influence on the aggregation behavior of NaDoBS in water that differs substantially from the aggregation behavior of NaDoBS in alkali metal chloride solutions. Initially NaDoBS remains in the micellar phase up to 0.03 *m* TBuACl and 0.9 *m* TMACl, addition of more salt at ambient temperature leads to phase separation into a surfactant-rich and surfactant-lean phase. At still higher salt concentrations (1.6 *m* for TBuACl and 2.2 *m* for TMACl), the clouding gradually gives way to a physically stable dispersion of unilamellar vesicles and multi*vesicular* vesicles, as can be clearly seen from Figures 3B and 4C. The vesicles are also nicely observable with CSLM (not shown); however, no bilayer undulations are found on the resolution scale of this technique, as was observed for the system described previously.[10] At high salt concentrations (TMACl, 3 *m*; TBuACl, 1.5 *m*) these vesicles are physically and colloidally stable for at least a year. Still higher salt concentrations (up to 7 *m* TMACl) lead to dissolution of the aggregates and no multilamellar aggregates are observed. More and more surfactant molecules are dissolved as monomers, and, of course, at 7 *m* TMACl (43% by weight) we can hardly speak of an *aqueous* solution anymore.

As was indicated by the fluorescence depolarization value *P*, the microviscosity inside the hydrophobic domains in the surfactant-rich phase is higher than in micellar aggregates but lower than in lamellar aggregates. Therefore, the packing of molecules is more regular and denser than in the micellar phase, but less than in a bilayer.

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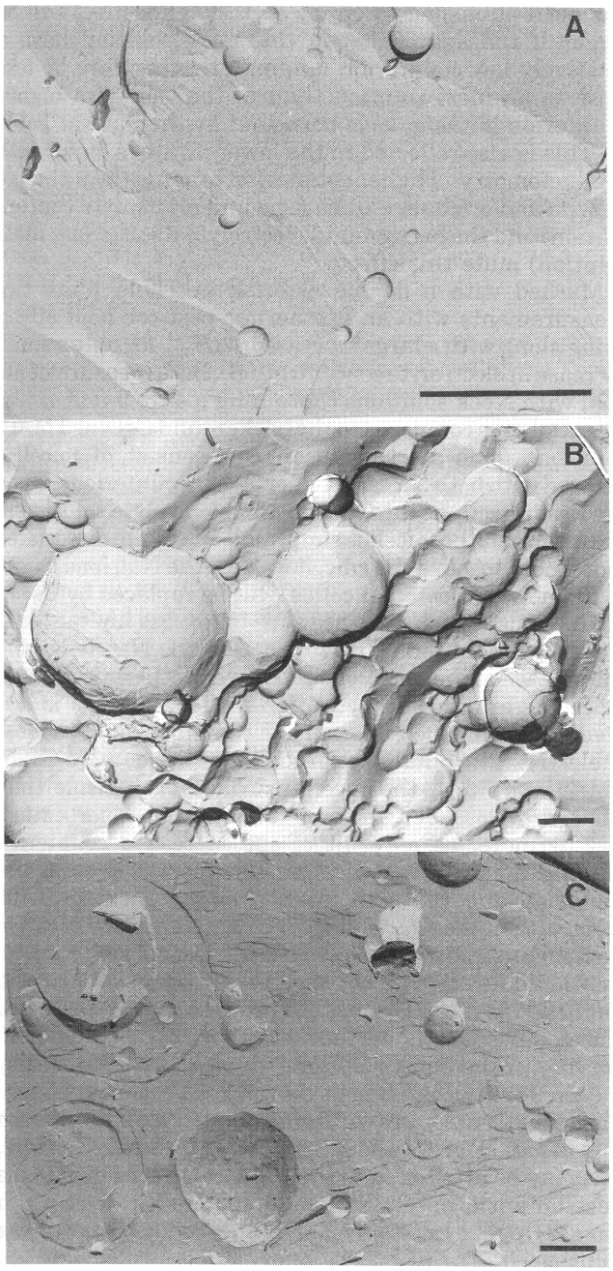

Figure 4. Freeze-fracture electron microsopy (FFEM) micrographs of (A) 2 m*m* NaDoBS in 0.1 *m* CsCl, unilamellar vesicles; (B) flocculated lamellar droplets (multilamellar vesicles) of NaDoBS in 1.2 *m* RbCl; (C) 4 m*m* NaDoBS in 3.3 *m* TMACl, large unilamellar and multivesicular vesicles. The bar represents 1 *m*m.

Similar characteristics were found in NMR line broadening experiments but will not be discussed here.

As can be inferred from Figure 2, most changes in aggregation type occur above 0.1 *m* salt concentration, that is always a 25-fold excess or more of bulk cations. (The only exception is TBuACl, for which phase changes occur at 0.03 *m*.) At this point it seems safe to assume that the bound Na^+ ions are exchanged substantially for the other cation X^+ (except for the LiCl case, see below). Information on the extent of the exchange can be obtained in the very dilute salt regime by conductivity and for a somewhat higher salt concentration with microcalorimetry. Listed in Table 1 are data obtained by those techniques. The values are extracted from raw data by models and calculations which are still under discussion.[24,25,29] Here the data are used predominantly to shed light on the difference in the behavior of cations and not on the absolute enthalpies, since that is not the object of this study. However, these absolute values are in rather good agreement with the literature data as far as available. cmc values for some pure sodium dodecylbenzenesulfonates are in the same range or vary similarly with salt concentration and the relatively small heat effects are also in accordance with the literature.[25,30,31]

Table 1. Critical Aggregation Concentrations, Enthalpies of Aggregation, and Fraction of Counterion Binding for NaDoBS in Electrolyte Solutions at 25.0 ± 0.1 °C (Unless Stated Otherwise)

solution	phase[a]	cac (mM)[b,c]	ΔH_{aggr} kJ/mol[c]	cmc (mM)[b]	b[d]
NaDoBS in water	mic	2.21	-0.9*	2.25	0.36
LiCl, 0.0035 M	mic	1.53	-0.8*	1.70	0.31
0.2 M	mic	0.17	-1.2*		
NaCl, 0.0035 M	mic	1.30	-1.2*	1.36	0.34
0.01 M	mic	0.73	-1.5		
0.05 M	mic	0.28	-2.2		
0.1 M	mic	0.23	-2.2		
0.2 M	mic	0.16	-2.5		
0.3 M	mic	0.12	-2.6		
KCl, 0.2 M	lam	0.15	-5.0		
RbCl, 0.2 M	lam	0.15	-6.0		
CsCl, 0.0035 M	mic	0.96	-2.4**	1.53	0.43
0.01 M	mic	0.55	-2.9		
0.05 M	mic	0.27	-4.7		
0.075 M	lam	0.21	-5.5		
0.1 M	lam	0.20	-6.7		
0.15 M	lam	0.14	-6.8		
0.2 M	lam	0.11	-6.5		
0.3 M	lam	0.09	-6.9		
TMACl, 0.0035 M	mic	0.82	-2.9**	0.97	0.38
2.0 M (2.65 *m*)	lam	0.07	-5.7		
CsDoBS in water	mic	1.55	-4.3	1.53	0.43
TMADoBS in water	mic	1.45	-3.9	1.61	0.40
5/6 NaDoBS, water	mic	1.80	+2.4!*	2.39	0.26
idem, 35 °C	mic	2.28	-4.9*		
idem, 45 °C	mic	2.07	-11.0*		
0.2 M NaCl	mic	0.13	-4.4		

[a] Type of aggregate, micellar or lamellar. [b] Critical aggregation concentration determined by microcalorimetry; critical micelle concentration determined by conductometry. [c] Errors in the values for ΔH_{aggr} and cac are usually less than 10 and 5%, respectively, for cac values below 0.2 mM the absolute heat effects are becoming quite small leading to error margins that can be as large as 25%. *, Pre-cmc slope, see text; **, negative post-cmc values, see text. [d] Fraction of counterions bound to the aggregate surface.

What do the values of the enthalpy of aggregation, ΔH_{aggr}, represent? In the titration experiment, a stock solution of surfactant at a concentration of 10 to 20 times the critical aggregation concentration (cac) either in water or in a particular salt solution is injected stepwise into a reservoir containing the same continuous phase, either water or an isotonic salt solution. This procedure gives rise to two heat effects: (i) dilution of a concentrated solution with surfactant aggregated either in micelles or in vesicles, depending on type and concentration of salt; (ii) deaggregation.[29] When the concentration in the reservoir has reached the cac, the heat effect caused by the deaggregation will vanish, leaving only the effect of dilution. Typical examples of raw data from a microcalorimetric experiment and subsequent data processing details have been shown by Bijma *et al.*[24] and van Os *et al.*[25]

The heat of dilution of a concentrated surfactant solution has been taken constant over the entire range of surfactant

(29) Mehrian, T.; Keizer, A. de; Korteweg, A. J.; Lyklema, J. *Colloids Surf. A* **1993**, *71*, 255.
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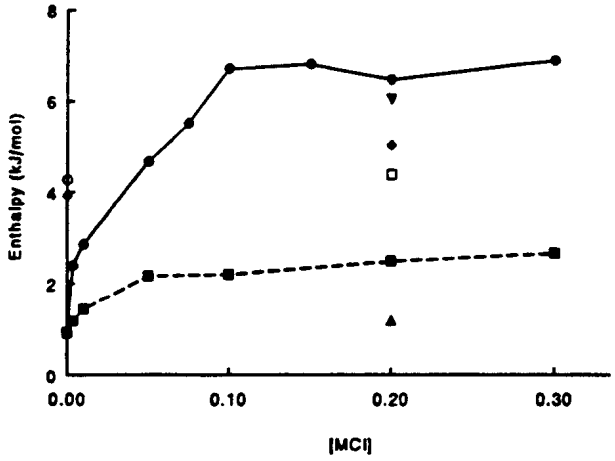

Figure 5. Enthalpy of aggregation (kJ/mol) for NaDoBS in (▲) 0.2 M LiCl, (■) in NaCl, (◆) in 0.2 M KCl, (▼) in 0.2 M RbCl, (●) in CsCl, (❑) isomerically pure 5/6 NaDoBS in 0.2 M NaCl, (❍) CsDoBS in water, and (✧) TMADoBS in water.

concentration examined. Formally this is not correct, because the first injection will show a rather high dilution effect, finally going to zero after an infinite number of injections when the concentration of the stock solution and in the reservoir have become equal. However, the practical error introduced by this interpretation is negligible.

The heat effect caused by deaggregation is the reverse of the effect of aggregation ($\Delta H_{deaggr} = -\Delta H_{aggr}$). Consider the effect of aggregation occurring at the cac: the driving force for surfactant aggregation is a delicate compromise of entropic and enthalpic contributions. The exact nature of this driving force, hydrophobic bonding, remains a point of debate in the literature.[32] The enthalpic parts of the aggregation process can be divided into several exothermic and endothermic contributions. The exothermic contribution predominantly stems from the dispersion forces which bind the hydrophobic tails in the core of the aggregate. For various aggregate morphologies this favorable enthalpy contribution will be different and will increase going from sphere- to rod-[33] to disk-like micelles and finally to lamellar aggregates.

The building up of an electrical double layer around the aggregate involves an important endothermic contribution. It originates from the repulsion of bringing the headgroups together and an endothermic contribution of the (entropy driven) build up of the diffuse part of the electrical double layer. The endothermicity will decrease further if the surrounding medium is an electrolyte solution and if the counterion binding is high. Moreover, the less hydrated counterions, that display a higher counterion binding, require less enthalpy for partial dehydration upon binding to the aggregate surface.

Many of the above mentioned features are reflected in the data in Table 1. Figure 5 is a compilation of the data in this table. The observed heat effects are relatively small, but fairly well reproducible, due to the high sensitivity of the microcalorimeter. This sensitivity also illuminated a slope in the heat values obtained for injections before the cmc for several samples (marked with one asterisk in the table). This is an indication of a difference in electrostatic interactions between surfactant molecules in the concentrated stock solution and dissociated monomeric surfactant molecules in the dilute solution in the reservoir. A detailed interpretation of this feature has been published by Bijma *et al.*[34] This effect will be larger if the aggregates in the stock solution have a relatively low counterion binding and therefore be less close to an ideal solution than in the case of a higher counterion binding, as is borne out by the data in Table 1. This is also reflected in the lower b values found with conductometry. Higher counterion binding (by a change in type and/or change in background electrolyte concentration) and the background electrolyte itself (a less ideal solution) mute this effect.

Marked with a double asterisk in Table 1 are two measurements with an exothermic post-cac heat effect, going along with a large increase in ΔH_{aggr} for only a small increase in electrolyte concentration. Both measurements deal with stock solutions containing a 4- to 9-fold excess of NaDoBS as compared to the background CsCl or TMACl solution. This stock solution will consist of micelles dressed with both Na^+ and Cs^+ or TMA^+ counterions. Upon the first injections into the 3.5 mM electrolyte solution in the reservoir, the micelles simply fall apart into dissociated monomers. Above the cmc, however, the Na^+ ions bound to the newly injected micelles, will be replaced by Cs^+ or TMA^+ ions which are present in excess in the bulk electrolyte solution. The removal of the Na^+ ions from the surface of the micelle will be an endothermic process, since the exothermic hydration of the Na^+ ions is less favorable than the endothermic contribution of the loss of electrostatic binding. On the other hand, more Cs^+ or TMA^+ ions bind to the micellar surface (exothermic) than Na^+, with less dehydration (endothermic) per cation. Furthermore, as a result of the increased counterion binding, the surfactant headgroups experience overall less repulsion and this will allow a better packing of the molecules in the aggregate. The overall process of cation exchange will be exothermic, as is borne out by experiment. Another indication for the exchange of bound Na^+ ions for Cs^+ or TMA^+ is the absence of a pre-cmc slope as discussed above, since this is an indication for higher counterion binding in the stock solution, which must be caused by the preferential binding of Cs^+ or TMA^+ ions. A similar conclusion can be drawn from conductometry, although this is less clear for the 3.5 mM TMACl case. However, this may be attributed to the TMA^+ ions that bind to the micellar surface, releasing more mobile Na^+ ions, which have a higher contribution to the conductivity of the solution.

A higher counterion binding is also apparent for both CsDoBS and TMADoBS in water: the ΔH_{aggr} is about 3 kJ/mol more favorable than for NaDoBS. This is readily reconcilable with the absence of a premicellar slope in the enthalpogram and with the higher b value obtained by conductometry.

A remarkable result is the endothermic ΔH_{aggr} for the isomerically pure 5/6 NaDoBS in water at 25 °C, illustrative for the importance of a positive entropy of aggregation as the driving force for aggregation. This endothermic effect can (at least partially) be explained by the significantly lower counterion binding (b = 0.26). This will give rise to a highly charged (thus enthalpically unfavorable) electrical double layer around the micelle, although isomeric purity would facilitate better packing and thus grant a more exothermic contribution to the ΔH_{aggr}. Going to higher temperatures, ΔH_{aggr} for 5/6 NaDoBS turns exothermic, as is commonly encountered for a variety of surfactants.[24,25,29,32]

Overall, the data in Table 1 show that lamellar aggregates formed from the dodecylbenzenesulfonate

(32) Blokzijl, W.; Engberts, J. B. F. N. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1545.
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Table 2. Characteristic Features of the Cations and Their Chloride Salts in Aqueous Solutions

Ion	hydration number *a*	hydration number *b*	hydrated radius (nm)[b]	relative osmolality[c]	refractive index[d]
Li^+	7.4	5-6	0.38	1.123	1.3416
Na^+	6.5	4-5	0.36	1	1.3427
K^+	5.1	3-4	0.33	0.932	1.3424
Rb^+	4.7		0.33		1.3427*
Cs^+	4.3	1-2	0.33	0.907	1.3452
TMA^+	1.8	0	0.37		1.3471*
$TBuA^+$	0.0		0.47		1.3695*

[a] Derived from limiting partial molar ionic volumes, data from Marcus.[35] [b] Data from Iaraelachvili,[18] except for Rb^+ and $TBuA^+$, values calculated from limiting partial molar volume (hydrated, Stokes), taken from Marcus.[35] [c] Calculated osmolality of a 1.0 *m* XCl solution in water, relative to the value of a 1 *m* NaCl solution, taken from ref 37. [d] Refractive index of a 1 *m* XCl solution in water, calculated from values listed in ref 37 or (*) determined at 25 °C, ±0.0005, see Experimental Section.

surfactant possess values for ΔH_{aggr} which are higher than 5 kJ/mol at 25 °C, which is in contrast with the lower values found for the micellar aggregates of this surfactant. This relatively high value is primarily determined by the type of counterion (compare CsDoBS with "Na"DoBS in ≥0.1 *m* CsCl). The value of ΔH_{aggr} is determined to a lesser extent by a less endothermic contribution of the electrical double layer in salt solutions above 0.1 *m*, and by the type of aggregate, since London dispersion interactions are more favorable for lamellar aggregates than for micelles. The small increase in ΔH_{aggr} for the NaCl solutions as compared to water is attributed primarily to a higher counterion binding.

Particularly striking is the effect of LiCl on the enthalpies of aggregation: practically none! Probably surfactant micelles will still have a substantial number of sodium counterions bound to the aggregate surface, thereby leaving Li^+ ions in the bulk of the solution, even at relatively high LiCl concentrations. Also only a small counterion binding can be inferred from the substantial endothermic contribution to the ΔH_{aggr} due to the build up of the electrical double layer even at 0.2 M LiCl.

Discussion

Cations and their Hydration Numbers. How can the aggregation behavior of NaDoBS in different salt solutions be explained? The key lies in the hydration numbers of the cations used in this study. Unfortunately, the magnitude of the hydration number depends on the experimental technique used to determine this property.[18,35,36] Listed in Table 2 are some hydration characteristics of different ions, showing discrepancies between several reports in the literature, but the general trend appears to be clear: an increasing atomic number (and atom size) leads to a decreased hydration number, and a slightly decreased size of the hydrated ion. The less hydrated an ion, the better it binds to an oppositely charged surface.

Exchange of Counterion. To understand the influence of salt concentration and the nature of the cation on the phase behavior of dilute NaDoBS solutions, we consider the two equilibria given in Scheme 1, where $[RS^-]$ is the dodecylbenzenesulfonate surfactant molecule in an aggregate (micelle or lamellar aggregate) and X^+ the cation of the XCl salt added to induce the phase changes. Notice

Scheme 1

$$[RS^- Na^+] + X^+(aq) + Cl^-(aq) \rightleftharpoons$$

$$[RS^-] + Na^+(aq) + X^+(aq) + Cl(aq) \rightleftharpoons [RS^- X^+] + Na^+(aq) + Cl^-(aq)$$

that the equilibrium constants should be expressed in activities because these highly concentrated solutions are far from thermodynamically ideal. These equilibria are the main issues for explaining the aggregation behavior. Of major importance are (i) changes in counterion binding, (ii) dehydration of the headgroup as a consequence of the addition of a salting-out electrolyte, and (iii) the influence of a salt on the physical interactions between molecules and between aggregates. Formally we should also consider the exchange equilibrium of cations between the electrical double layer and bulk solution far away from the aggregate surface.

Aggregation Behavior on the Molecular Scale. The shape of the surfactant molecule primarily determines the aggregate morphology under equilibrium conditions. The geometrical effects can be expressed in terms of an experimental geometrical packing parameter[18] $P = v / al$, where v is the volume of the hydrophobic chain of the surfactant molecule, a is the optimal cross-sectional area that the hydrated headgroup occupies at the aggregate-aqueous phase interface, and l is the maximum effective length of the hydrocarbon chain in a fluid state. Included in the value for a are factors such as counterion binding and nonoptimal hydration of the headgroup when the solution conditions change, for instance by a salting-out electrolyte present in a high concentration or when the surfactant concentration is so high that it can form other lyotopic liquid crystalline phases. The surfactant used in this study is an important industrial product with many commercial applications and is not monodisperse; its dodecyl chain can be attached on any of the carbon atoms to the benzenesulfonate moiety. Therefore, the surfactant can be considered double-tailed, which usually leads to a bilayer-forming amphiphile. Sodium dodecylbenzenesulfonate, however, forms micelles in water, as also has been reported frequently in the literature, albeit with different micellar shapes.[25,28,30,38,39] Lamellar phases are formed only at higher surfactant concentrations.[40] Our results (*vide supra*) illustrate that when the counterion is changed toward a less hydrated type, and the counterion binding increases, electrostatic repulsions between headgroups can be overcome more easily. Moreover, dehydration of the headgroups and bound ions as a result of adding a salting-out electrolyte reduces the steric constraints. Both factors will facilitate aggregation in a lamellar array,[3] although we contend that an increase in counterion binding is a more important factor than dehydration.

The isomeric structure of the molecule can have a profound influence on the aggregation behavior. A comparison of the influence of NaCl on the aggregation behavior of the polydisperse NaDoBS surfactant with the isomerically pure 5/6 NaDoBS (see Figure 2B) illustrates the importance of the packing of the hydrophobic part of the amphiphile. Presumably, the packing mismatches for the polydisperse amphiphile allow the surfactant to aggregate in the more chaotic micelle up to a higher salt concentration than that for its isomerically pure analogue. This also illustrates that the packing parameter is less applicable to polydisperse surfactants.

(35) Marcus, Y. *Ion Solvation*; Wiley: Chichester, 1985.
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Also the length and volume of the hydrophobic moiety of the alkylbenzenesulfonate are crucial parameters which are hard to be accounted for correctly in the packing parameter. For a truly cylindrically shaped amphiphile, an increase in chain length cancels the increase in volume of the hydrophobic moiety, so that the packing parameter remains constant with increasing chain length. For a truncated-cone shaped amphiphile, as discussed here, the volume also scales with the length above a certain alkyl chain length. Nevertheless, an alkylbenzenesulfonate with a longer tail such as SHBS (sodium 4-(1´-heptylnonyl)benzenesulfonate) is known to aggregate in a lamellar arrangement in water,[41,42] whereas it has exactly the same topview as 5/6 NaDoBS and thus both surfactants will have a practically identical packing parameter. Nonetheless, 5/6 NaDoBS forms micelles in water. The influence of counterion binding has been illustrated nicely by the addition of a cryptand to a dispersion of SHBS in water.[43] The sodium counterion will be dragged away from the aggregate surface, giving way to electrostatic repulsions between the sulfonate headgroups and probably to an increase in hydration of the headgroups. This leads to a higher curvature of the aggregate surface and a concomitant dissolution of the lamellar aggregates into micelles.

Interactions between Lamellae and between Aggregates. As explained in the introduction, four factors dominate the interactions between aggregates and bilayers in particular: van der Waals attractions, electrical double layer repulsions, hydration, and thermally induced steric repulsions. The influence of salt on all these forces will determine the overall aggregation behavior, and different salts will display different influences. The attractive van der Waals force will be lower in electrolyte solution than in water. The van der Waals interaction of two bodies (here the bilayers or the different aggregates) acting across a different medium (the electrolyte solution) can be described by the Hamaker constant. This Hamaker constant is composed of two terms: a zero-frequency part and a nonzero or high-frequency part. Ions in aqueous solutions are too massive to follow high-frequency oscillations, and therefore will not influence the high-frequency contribution to the Hamaker constant; this term will be comparable for water and aqueous electrolyte solutions. On the other hand, the electrolyte solution will screen the zero-frequency contribution substantially (compared to water).[44] Moreover, this zero-frequency part is an important contribution to the Hamaker constant for hydrocarbons acting across aqueous media.[18,44] In our study, we address the question whether this decrease in van der Waals attraction at increasing salt concentration changes as a function of the *type* of cation dissolved in the interlamellar medium. This screening of the zero-frequency part is related to the number of electrons per ion, which is also a feature determining the refractive index of that particular aqueous electrolyte solution. Therefore it is expected that, at equal concentrations, different cations might cause different van der Waals attractions. However, whether this effect is large enough to be observed in practice, is not clear. This view is supported by the fact that the refractive indices hardly vary for 1 *m* alkali metal chloride salts (Table 2). Van der Waals attraction between bilayers consisting of alkylbenzenesulfonates can be large compared to attractions between bilayers built up of alkyl chains since London dispersion interactions between aromatic moieties are relatively strong due to the high polarizability of the *p*-system. This difference is also seen in the different refractive indices (and dielectric constants):[11] 1.482 *vs* 1.422 for dodecylbenzene and dodecane, respectively. Although the van der Waals attraction decreases at increasing electrolyte concentration, it obviously is the predominant interaction and does not decrease as much as all combined long-range repulsions since for all alkali metal cations, the attraction ultimately vindicates over repulsion, because flocculated multilamellar aggregates are finally formed in all cases.

On the repulsive side, hydration forces operate only over rather short distances (below 3 nm). Since the headgroups and most ions will not have the maximum number of solvating water molecules available at high electrolyte concentrations, hydration repulsions between surfactant aggregates will be appreciably less than in a purely aqueous environment. The Helfrich undulation repulsion can act over somewhat longer ranges,[18] especially if the bilayers are highly flexible, *i.e.*, possess a low bending modulus. Bilayer rigidity depends *inter alia*, on the thickness of the bilayer, which is rather low for a bilayer formed from NaDoBS molecules (*ca.* 1.9 nm[11]). There is no reason, however, to expect the bending modulus to change on increasing the background electrolyte concentration or changing the type of background electrolyte, except probably for a small contribution of a lower surface charge density for bilayers decorated with Cs^+ ions compared to Na^+ ions. Also peristaltic and protrusion factors operate over small distances (less than 3 nm), though no differences are expected for different type or concentration of background electrolyte, at least not for the alkali metal salts. For the TAA salts, protrusion might become a factor to take into account. Since these salts are salting-in electrolytes, monomer solubility increases and the interfacial tension decreases in a TAACl solution compared to water, leading to the possibility for the surfactant molecules to jump out of the lamellar layer.[21]

The origin of the electrical double layer forces lies in the balance between electrostatic and entropic forces of the dissociated counterions, leading to an osmotic repulsion when two, here negatively charged, aggregate surfaces approach. Increasing counterion binding and concomittantly decreasing surface charge density will decrease the electrical double layer repulsions. The electrical double layer repulsion depends on the difference between the number of cations in the double layer *vs.* the number of cations in the bulk electrolyte solution. Thus, an increase of background electrolyte concentration reduces this osmotic repulsion. An additional feature to take into account is the change in osmotic force when the cations in the positive layer vary from Li^+ to Cs^+. Would this lead to a drastic change in repulsion, would for instance Cs^+ give rise to a much larger osmotic repulsion? A comparison of the osmotic pressure values listed in Table 2 for several 1 *m* XCl solutions does *not* make this a tempting idea: a CsCl solution can exert an osmotic pressure which is only 91% of the osmotic pressure which is exerted by an NaCl solution of equal molal concentration. It is a small difference, but nevertheless, it acts in the wrong direction to explain the experimental observations (see also below).

The interactions between bilayers or aggregates as a function of interbilayer or -aggregate distance is a

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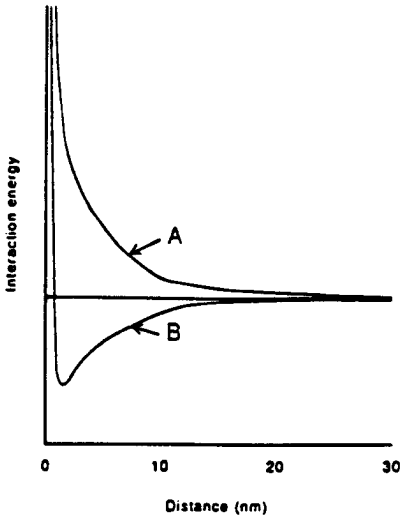

Figure 6. Interaction energy *vs* distance for surfactant aggregates acting across the aqueous electrolyte solution: (A) relative low salt concentration, lamellar layers (and separate aggregates) repel; (B) high salt concentration, lamellar layers (and aggregates) experience a net attractive force, in the case of flocculated multilamellar aggregates the equilibrium distance is approximately 1.5 nm. The depth of the well, shallow or deep, is also an important factor determining whether, respectively, unilamellar or multilamellar aggregates are formed. Repulsions at low distances (solvation and steric) prevent complete collapse and full squeezing out of water.

compilation of the forces mentioned above. We will both consider the interactions between bilayers in one aggregate (intraaggregate) and the interactions between bilayers of separate aggregates (interaggregate), as being of similar nature. The net interaction is pictured in Figure 6 for two extreme cases. Curve A represents the interactions experienced by bilayers where only repulsions are dominant. This state is sometimes called extremely swollen[11] or fully unbound.[45] Curve B pictures the case where attraction allows bilayers to approach each other until at short distance the repulsions take over. Thus multilayers or stacks of bilayers are formed and the aggregates tend to flocculate. This entropically unfavorable state occurs at relatively high alkali metal chloride concentrations, where strongly flocculated multilamellar droplets are formed and separate from the electrolyte solution (Figures 3C,D and 4B). In this case the depth of the minimum must be rather large as it cannot be overcome by thermal motions. The distance where the minimum occurs, is sketched, *i.e.* at 1.5 nm, is a crude approximation, derived from calculations performed by van de Pas.[11] That indeed this will be a small value can be inferred from FFEM.[10,11]

Five Different Cases for Electrolyte-Induced Effects on Surfactant Aggregation. We return to Scheme 1 in an attempt to explain the differences in aggregation behavior as discussed above. Five cases will be considered: (i) no electrolyte added; (ii) NaCl solutions; (iii) solutions with alkali metal cations with a higher atomic number than Na^+; (iv) LiCl solutions; (v) tetraalkylammonium chloride solutions.

(i) No Electrolyte. In plain water only the left-hand side equilibrium (Scheme 1) matters but counterion binding will be low. Therefore, large electrostatic and hydration repulsions between surfactant headgroups occur, leading to the formation of micelles. In terms of the packing parameter analysis, these micelles will be nonspherical.

(ii) NaCl Solutions. Again only the left equilibrium (Scheme 1) matters. However, this will shift more and more to the left-hand side as the NaCl concentration increases. Furthermore, the entropic (osmotic) force to maintain the electrical double layer will diminish if the background electrolyte concentration increases. A higher counterion binding will result. At higher concentrations, the salting-out property of NaCl will tend to dehydrate all ions, particularly the surfactant headgroups. As a result of both the higher counterion binding and partial dehydration, surfactant headgroups can be packed more tightly, leading to packing in a lamellar array at 0.3 *m* NaCl concentration. The van der Waals attraction probably increases substantially when the aggregate structure changes from micelles to lamellar aggregates. This can be due to two factors: the lamellar aggregates are larger and possess a closer molecular packing than the micelles. At this point the interlamellar van der Waals attraction is now suddenly large enough to overcome the repulsions (predominantly the electrical double layer repulsion), resulting in the formation of flocculated multilamellar aggregates. How delicate this simultaneous change in packing and the change in magnitude of the repulsions is can be inferred from the fact that the isomerically pure 5/6 NaDoBS shows at the same NaCl concentration a unilamellar region where relatively large repulsions operate although the molecules are already in a lamellar arrangement. In addition, the unilamellar to multilamellar transition occurs at lower salt concentration (0.25 *vs* 0.30 *m* for 5/6 NaDoBS and the polydisperse analogue, respectively, see Figure 2B); thus the van der Waals attraction between 5/6 NaDoBS lamellae will be slightly larger than for polydisperse commercial surfactant.

(iii) KCl, RbCl, or CsCl Solutions. For all the other salts the right-hand side equilibrium comes into play. As was illustrated by microcalorimetry and conductivity, this effect will play a crucial role already at low concentrations of KCl, RbCl, and CsCl. Going from Na^+ to K^+ to Rb^+ to Cs^+, *i.e.*, going toward less hydrated cations, the equilibrium will shift more and more to the far right hand side, induced by increasingly favorable counterion binding. At relatively low salt concentration, Na^+ will be preferably depleted as a counterion (see for instance the large heat effects for the 3.5 mM CsCl experiment, Table 1). The increased counterion binding will lead to decreased interheadgroup repulsions, and going toward Cs^+, the surfactant molecules have a propensity to aggregate in lamellae at decreasing concentrations of added salt. Large unilamellar vesicles are formed (Figures 3A and 4A), with a net repulsion between lamellae and between vesicles. The slow sedimentation points to a physically instable dispersion, gravity can overcome the dispersive action between the aggregates, vesicles precipitate but do not fuse or turn into multilamellar structures. The interaction is probably well described by curve B in Figure 6, with a minimum so shallow that thermal motions can keep the aggregates apart.

The transition from unilamellar to multilamellar aggregates occurs at an increasingly higher concentration of added electrolyte, upon going from Na^+ to Cs^+. Since the van der Waals attraction decreases with salt concentration largely independent of the *type* of alkali metal cation, the dominant factor inducing the *differences* in unilamellar to multilamellar transition will be repulsive in nature. Furthermore, the type of alkali metal cation will not noticably influence the steric repulsions, and since these repulsions operate only over small distances, these effects can be neglected in a first approximation. The possibility to dehydrate the headgroup will decrease going from NaCl toward the CsCl, so the hydration repulsion will become larger going into that same direction, albeit that this repulsion operates over fairly small distances.

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As discussed before, the osmotic pressure and surface charge density decrease going from a double layer with Na^+ ions to one with Cs^+ as the counterions. Thus, a lower electrical double layer repulsion is expected for Cs^+ relative to Na^+. This therefore cannot explain the experimental observation that the transition from unilamellar to multilamellar aggregates occurs at a *higher* salt concentration for CsCl as compared to NaCl (Figure 2A). Lowering the surface charge density by changing to Cs^+ as counterions instead of Na^+ or by increasing the electrolyte concentration will lead to more flexible bilayers and a concomitant increased undulation repulsion. This, however, cannot be a dominant factor since at higher electrolyte concentration the van der Waals attractions obviously can overcome the repulsions, and undulation repulsions are only expected to increase, if they change at all. What remains as an explanation? Left out of the discussion thus far is a possible contribution due to the hydrophobic attraction between bilayers, or more particularly, between parts of the hydrophobic tails that are exposed to water.[18,32,46] It is reasonable to expect a higher hydrophobic attraction between bilayers with a relatively low number of bound counterions (the Na^+ case), which shield the hydrophobic interior less effectively than, for instance, the case with high counterion binding (Cs^+).

(iv) LiCl Solutions. For the strongly hydrated Li^+ ion, hydration repulsion may be a more important factor.[47] At relatively low concentrations, Li^+ has only a minor effect on the position of the equilibria shown in Scheme 1. Only at higher LiCl concentrations can a shift toward the right-hand side be expected, which is due simply to the large excess of Li^+ (i.e. at 1 *m* LiCl and 4 m*m* NaDoBS, a 250-fold excess). Thus at a relatively high concentration of LiCl, a small counterion binding is still expected. If a cation binds, it most likely will be a Li^+ which drags along a considerable hydration shell. We contend that even at high concentrations of LiCl, micelles with highly curved surfaces will remain. A similar effect has been observed for strongly hydrated ions as hydroxide and acetate, inducing enhanced bilayer curvature of (positively charged) didodecyldimethylammonium bromide (DDAB) lamellae.[3,48] Nonetheless, along with the increasing LiCl concentration also the electrical double layer repulsion will disappear and at 1.1 *m*, the van der Waals attractions between micelles will triumph over repulsions, and the micelles will phase separate from solution before packing in a lamellar array has been completed. Further addition of LiCl leads to further dehydration of the headgroups and all other ions. At these high salt concentrations, even the hydration of the Li^+ ions in the bulk will decrease, which facilitates higher counterion binding, giving way to less steric constraints and less electrostatic repulsions between headgroups, with ultimately, the formation of a lamellar arrangement of the surfactant molecules. However, the interaggregate repulsions have already been overcome and therefore only multilamellar aggregates form, which flocculate and precipitate. This idea is supported by the increase in the fluorescence depolarization value *P* over the concentration range where the phase separation occurs.

(v) TAACl Solutions. The aggregation behavior in tetraalkylammonium chloride (TAACl) salts is remarkable. It seems clear that an explanation as given above for the behavior of NaDoBS in aqueous alkali metal chloride salt solutions does not apply here. The tetraalkylammonium ions, particularly the $TBuA^+$ ion, have a salting-in character and enhance the solubility of otherwise poorly water-soluble compounds.[49] One clue, delivered by microcalorimetry, is the high counterion binding. Compared to the other cations, the TAA ions are poorly hydrated and therefore will have only limited objections against binding to the micellar surface. On the other hand, the ions have a low charge density. The right-hand side equilibrium (Scheme 1) shifts farther to the right and becomes dominant, the effect being larger for $TBuA^+$ than for TMA^+ ions. As a result rather hydrophobic particles will be created, which, in first instance, do not dissolve in the dilute aqueous TAACl solution. The aggregates phase separate, probably with the withdrawal of several water molecules still sticking to the polar surface of the aggregate. Only at higher TAACl concentrations can the salting-in character of TAACl become an important factor. As a consequence, the propensity of the headgroups to remain in contact with the aqueous electrolyte solution increases as the TAACl concentration increases. Since the tails still prefer to be in a hydrophobic domain, bilayers are formed, resulting in the physically and colloidally stable large vesicles (uni- and multi vesicular), shown in Figure 4c. The physical origin of the high bilayer-bilayer repulsion remains enigmatic. Confocal scanning laser microscopy provided no evidence for the enormous Helfrich undulation of the bilayers as observed before for the large vesicles formed from a mixture of NaDoBS and a nonionic surfactant in 10% (w/w) sodium citrate solution.[10] Probably, the van der Waals attraction is too small to overcome repulsions (the refractive index of a 1 *m* TBuACl solution in water is higher than for water or aqueous solutions of the other salts). On the other hand, due to the high counterion binding, the electrical double layer repulsion will be low, too. In view of the complex situation, it is clear that more work will be necessary to fully understand the behavior of TAA cations in surfactant systems. A similar temperature-dependent phase separation phenomenon of ionic surfactants has been described in the literature, both in aqueous[50] and in electrolyte solution.[51] One common factor in these reports is that they all deal with quaternary ammonium salts. Jansson *et al.*[52] have also observed a strong counterion binding of TAA cations to anionic surfactants. Their observation was related to the destabilization of emulsions by the addition of TAA cations, particularly $TBuA^+$. It was suggested that not only electrostatic factors should be considered and that, although bound, the bulkiness of the TAA ions (Table 2) led to ineffective screening of the headgroup-headgroup repulsions at small aggregate curvature. A similar explanation was suggested by Wagenaar *et al.*[27] to account for the lower gel-to-liquid crystalline phase transition for TMA-dihexadecyl phosphate vesicles, as compared to the corresponding Na^+ salt. In addition, Kachar *et al.*[42e] state that the tetraethanolammonium counterion is located farther out from the surface of a 4-(1´-heptylnonyl)-benzenesulfonate aggregate, inducing noticable curvature of the bilayer surface. Finally, Jansson *et al.*[52] argue that attractive hydrophobic interactions occurring between emulsion droplets are enhanced with the adsorption of

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these hydrophobic ions. A similar explanation is obviously not valid here, since the observed vesicles will indeed have a highly hydrophobic surface, with TAA cations bound to the surface, but still a large repulsion must exist (curve A in Figure 6) since no sign of aggregation is observed over a period of a year.

Transition between Aggregates on a Molecular Scale. A final remark on the observed transitions from one type of aggregate to another on a molecular scale seems in order. The formation of unilamellar vesicles can be attributed to an initial change in micellar shape, upon increasing salt concentations toward a rod- or disklike micelle. The size of the aggregate will then grow dramatically, turning to a large flat aggregate, a pancake structure or a bilayer fragment, which will close spontaneously to form large unilamellar vesicles. This spontaneous closure is induced by thermal fluctuations of the bilayer pancake, the driving force can be the minimization of edge effects.[53]

It is remarkable that at higher salt concentrations the unilamellar vesicles do not aggregate (flocculate) but transform to multilamellar aggregates, which subsequently flocculate and fall out of solution. This transition from unilamellar to multilamellar aggregates must involve enormous rearrangements of molecules between different layers. In this process, we envisage passages in which whole patches of lamellarly arranged molecules protrude from one bilayer and insert into another. Local instabilities in the bilayer and local packing mismatches, both amplified by undulation and peristaltic motions of the bilayer and by potential differences arising from salt concentration differences between solution inside and outside a vesicle, could be nuclei for short lived intermediate structures, resembling temporary L_3 phaselike bicontinuous structures with bilayer curvature in both directions. These bypasses presumably will facilitate the flow of surfactant molecules from one bilayer to the other.

Conclusions

The formation of a lamellar phase from the micellar phase of the anionic surfactant sodium dodecylbenzenesulfonate (NaDoBS) in dilute solutions can be induced by various alkali metal chlorides and tetraalkylammonium chloride salts. A distinction has to be made between the influence of salt on a molecular scale and on a larger scale, *i.e.* the aggregate level.

On a molecular level, an increase in alkali metal cation concentration induces the packing of molecules into a lamellar array, which is facilitated by an increase in counterion binding and to a lesser extent by dehydration of the headgroups induced by the addition of a salting-out electrolyte. Both effects will facilitate a closer packing of the surfactant headgroups, which leads to the rearrangement from micelles into lamellae. An excess of foreign ion X^+ will replace Na^+ as the counterion, as illustrated by Scheme 1. An exception is the highly hydrated Li^+ ion which at low concentrations is not capable of replacing the Na^+ ion. The observed transformations of the assemblies can be described as the phase behavior of the surfactant XDoBS in XCl solution. A change toward a less hydrated ion X^+ parallels an increase in counterion binding. This translates into the packing in a lamellar array which occurs at a decreasing electrolyte concentration going from LiCl to CsCl.

On the aggegate level, the interactions between lamellar layers and between aggregates lead to the formation of large unilamellar vesicles when long range repulsions are stronger than attractions (curve A in Figure 6) and to flocculated multilamellar vesicles, called lamellar droplets, when bilayers and aggregates experience an attractive force down to a short distance, when short range repulsions take over (curve B in Figure 6). Figure 2A summarizes the observed phases as a function of salt for dilute NaDoBS solutions. Electrostatic double layer repulsions are expected to be smaller when the surface potential is lower, which is expected for high counterion binding. In addition, the osmotic repulsion is expected to be lower for a double layer consisting of Cs^+ ions as compared to the Na^+ case. It is argued that other interactions do not change significantly by a change of the type of cation. In contrast to expectations, the phase behavior in CsCl shows strong long range repulsions up to the highest concentration. A possible explanation for this paradox, lies in a lower hydrophobic attraction between bilayers and between aggregates for the situation where Cs^+ ions are bound to the bilayer surface (compared to the Na^+ case), or a lower van der Waals attraction between two bilayers acting over a CsCl solution, compared to a NaCl solution of equal molality.

Between 1.1 and 1.6 *m* LiCl, dilute NaDoBS solutions phase separate into a surfactant-rich and a surfactant-lean phase. At higher LiCl concentrations, regular flocculated lamellar droplets are formed. The surfactant-rich phase is formed when the interaggregate attractions can overcome repulsions, even before the molecules can pack in a lamellar array.

The phase behavior in tetraalkylammonium chloride salt solutions appears to be a regular cloud point phenomenon as is observed for nonionic poly(ethylene oxide)-based surfactants. The behavior is rationalized by a high counterion binding which creates a rather hydrophobic moiety, which causes a high attraction between the surfactant aggregates and leading to phase separation. At higher TAACl concentrations, the salting-in effect increases the headgroup solubility, leading to stable dispersions of large unilamellar and multivesicular vesicles.

The difference between the phase behavior of the polydisperse NaDoBS and of the isomerically pure 5/6 NaDoBS (Figure 2B) illustrates the importance of the packing of the hydrophobic tails in a lamellar arrangement, which is hampered by the polydispersity of the alkyl chain.

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